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WHY DO GLASSY MATERIALS POSSESS ENERGY GAPS?(U)
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(6) Why Do Glassy Materials Possess Energy Gaps? *

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Jim

This is a question which has long been an embarrassment to the physicist. Modern solid state physics had its beginnings in the initial theoretical triumph in which forbidden energy regions (gaps) were predicted by Bloch and Wilson as following from the symmetry properties of crystals. Mott and Davis¹ (MD) were among the first to consider the problem seriously and have provided an argument which, although generally accepted, remains enigmatic.

The amorphous covalent semiconductor provides a case in point. MD were inclined to reject the conjecture proposed by Cohen, Fritzsche and Ovshinsky² (CFO) that the underlying disorder is likely to remove the gap completely. This picture would smear the conduction and valence bands of the corresponding crystalline material into the gap producing a finite density of states $N(E_F)$ at the Fermi energy E_F . These authors relied on the qualitative feature of states in the gap continuum, namely, that their corresponding wavefunctions are Anderson localized, in order to reproduce the experimental similarities to crystals. However, about the same time (~1970), Mott deduced³ the finite frequency conductivity $\sigma(\omega)$ expected for a band of localized states. The real (absorptive) part $\sigma(\omega)$ was found to behave as ω^2 at low temperatures so that even including matrix elements effects no absorption gap occurs. Typically, for a-Si and a-Ge, gaps are deduced, for annealed films, to be somewhat higher than in their corresponding crystals. For insulating glasses, gaps can range to ~10eV. Moreover, there have been no reported observations of ω^2 absorption in any system.

The basic assumption of MD's model is that short range structural properties make the largest contribution to the overall spectral density. It is well known that a wide range of amorphous materials with crystalline phases demonstrates significant short range order. Thus, MD argue that

much of the spectral structure, including gaps, should be preserved. Recent numerical studies, which do not rely on Bloch's theorem, tend to support this point of view. Indeed, it is easy to demonstrate⁴ the existence of exact energy gaps for simple models without long-range order. The common approximation of all these studies, however, is to ignore or truncate the distribution of matrix elements contributing to the spectral density.

The enigma is apparent when electrical properties are considered. Again, we restrict ourselves to the semiconductor. A more or less universal property of amorphous semiconductors is that they are not "intrinsic". That is, the position of E_F is not determined by the states in the conduction or valence band. The overwhelming evidence is that $N(E_F)$ is indeed finite and that E_F is pinned (against doping) at about mid-gap. This has led Davis and Mott to propose⁵ a "defect band" in which a band of states is introduced near mid-gap so that $N(E_F) \neq 0$. The density of these states is adjusted so that E_F remains pinned (large) but they remain non-absorbing vis a vis ω^2 (not too large). The authors note, however, that no explanation is provided for the location of this band near mid-gap.

This somewhat unsatisfactory state of affairs prompted Anderson to propose⁶ a different mechanism for transparency. Anderson argued that the glassy state was characteristically diamagnetic, so that unpaired spins (electrons) were unfavored. The model introduces an effective negative correlation energy $-\tilde{U}$ which couples electrons located at the same site. The attractive part, denoted by C , is mediated by the electron-phonon interaction which may be appreciable in glassy systems where soft phonon modes are known to exist from independent thermodynamic measurements. In the case in which $\tilde{U} \equiv C - U > 0$, where U is the on-site repulsive part (Hubbard) of electronic correlation, diamagnetism and an absorptive gap

follow. This situation is not unlike that which occurs in superconductivity where infrared transparency occurs for temperatures below T_c . In the glass, the energy scale is expanded by a factor $10^3 - 10^4$ so that much stronger correlations are indicated. In addition, Anderson assumed the disorder is severe so that $N(E) \neq 0$ for all E where E is the unrelaxed site energy for a single electron.

⁷
Mott, Davis and Street and others have borrowed the negative \tilde{U} idea in discussing the nature of the defect states for the class of chalcogenide semiconducting glasses. This permits a much larger density of defects to account for the strong pinning in these systems without introducing an absorptive mechanism. Nonetheless, recent optical and transport measurements⁸ performed on the same doped samples of these materials have cast serious doubt, in my opinion, on the validity of a simple defect picture, at least for these systems.

It is worthwhile, however, to examine these perspectives in more detail. A more general observation suggested by the negative \tilde{U} defect state is that the value of \tilde{U} for a particular state (site) may bear some relationship to the corresponding one-electron energy, i.e. to where the state lies within the spectrum. That is, Mott et al.⁷ employed the negative \tilde{U} idea selectively for those states which resulted from deviations from typical local structures. Anderson introduced no such prejudice although some correlation⁹ certainly exists between the degree of localization and the magnitude of \tilde{U} . We provide here an extreme example in which we examine the Anderson negative \tilde{U} model but allow for a specific correlation among the site parameters.

We consider a random distribution (in space and in energy) of localized states; no structure, e.g. gaps, is presumed to exist in the

energy spectrum. In the ground state, half are occupied by two electrons. Of course, the most obvious doubly occupied localized state in a covalent material is the bond which, however, consists normally of two states, bonding σ and antibonding σ^* . It is convenient to characterize these states by their one-electron, unrelaxed energies which we denote, respectively, $E_i^\sigma < 0$ and $E_i^{\sigma*} = -E_i^\sigma$ for the i^{th} bond. Thus we explicitly consider two states per site (bond). The symmetry about $E_i = 0$ is taken only for convenience. Setting the one-electron fermi energy $E_F = 0$, we insure that only the bonding state is occupied in the ground state.

Following Anderson, a linear electron-phonon interaction is introduced, reducing the energy of the i^{th} bonding state (or antibonding state) by a quadratic term $-\frac{1}{2} C_i n_i^2$ in the electron occupation n_i . Allowing also for a repulsive term $U_i \delta_{n_i,2}$ for the coulomb interaction, the true bonding energy for a doubly occupied site is

$$E_{2e} = 2E_i^\sigma + U_i - 2C_i \quad (1)$$

Thus, in general, each site is characterized by the three parameters E_i , U_i , and C_i where we assume the antibonding state (with energy $-E_i^\sigma > 0$) at the site i shares the same values of C_i and U_i .

The values of both C_i and U_i are largely dependent on the degree of localization and should behave roughly as $|\psi_i|^{-4}$ where ψ_i is the one-electron localized wave function. If we assume both scale with $|\psi_i|^{-4}$ aside from an overall constant, then we may define $U_i = g C_i$ where $g < 1$ by assumption. In addition, localization can be expected to be more severe near E_F (or, in a semiconductor language, for deeper levels). This immediately suggests that C_i (and U_i) is a monotonically decreasing function of $|E_F - E_i|$. For simplicity, we assume the linear relation

$$E_i^{\sigma*} = E_c - (E_c/C_{\max})C_i \quad (2)$$

for $E_i^{\sigma*} > 0$ or anti-bonding-like states and

$$E_i = E_v - (E_v/C_{\max})C_i \quad (3)$$

for $E_i^{\sigma} < 0$ or bonding-like states. E_c and E_v are the mobility edges, i.e. energies where $|\psi_i|^{-4} = 0$ in the conduction and valence bands, respectively. Equations (2) and (3) are written so that the site with the largest coupling C_{\max} occurs at the fermi energy $E_F = 0$. The linear assumption is certainly an oversimplification near the mobility edges where the wave function behaves like $\psi(r) \sim \exp(-(E-E_{c,v})^\eta r)$ where η is not known exactly but various estimates give roughly .6.

Accordingly, we may deduce the optical absorption expected from a system with these properties. The states we consider are severely localized and we allow for optical matrix elements only between the two states at the same site. Thus we examine the excitation of an electron from σ to σ^* at site i unless the absorption energy is sufficient to connect the mobile states i.e. larger than $E_c - E_v$.

Let us evaluate the absorption energy ϵ for this process. The excitation we envisage is depicted in figure 1 in an energy-configuration diagram for the site i . The higher energy curves relate to the antibonding state σ^* and the lower curves correspond to σ . We must consider two contributions: 1) the energy to add an electron (without configurational relaxation) to the empty antibonding state. The excitation is indicated by a vertical arrow in which the occupation for the σ^* state changes from $n_i = 0$ (state labeled (0)) to $n_i = 1$ (state labeled (1)). The energy for the process is $E_i^{\sigma*}$ according to our definitions given above.

2) the energy to change the occupation of the bonding state σ from $n_i = 2$ to $n_i = 1$. The excitation is shown in Figure 1 for the σ configurational levels. Note that the states are configurationally displaced according to occupation due to the inclusion of the electron-phonon terms in the model. The energy for the second process must take account of the energy of the doubly-occupied bonding state given by (1). Using the relation $U_i = gC_i$ and combining the two processes we have for the absorption energy at the site i ,

$$\epsilon_i = E_i^{\sigma*} - E_i^{\sigma} + (2-g)C_i \quad (4)$$

Substituting (2) and (3) we obtain

$$\epsilon_i = E_c - E_v + [(2-g) - (E_c - E_v)/C_{\max}]C_i \quad (5)$$

This result is very interesting. It predicts that the absorption edge, i.e. $\min \epsilon_i$, does not necessarily result from pairs of electrons whose one-electron states are at E_F (where $C_i = C_{\max}$). This is the case for a strongly coupled system in which $(2-g)C_{\max} > E_c - E_v$. In this instance, the minimum energy for absorption is given by $\min \epsilon_i = E_c - E_v$ so that photoexcitation between mobile (conducting) states occurs at the absorption edge. This should be reflected in the photoconductivity and in the steepness of the absorption edge. MD have remarked on the sharpness of some optical data in glassy systems but have attributed it to the relaxation of selection rules for the amorphous case.

The result is summarized in Figure 2 where we distinguish a strong coupling system (a) corresponding to $(2-g)C_{\max} > E_c - E_v$ and a weak coupling system (b) corresponding to $(2-g)C_{\max} < E_c - E_v$. The diagrams

relate the single-particle energy E_i to the lattice coupling C_i according to the simple linear model introduced in equations (2) and (3). The σ^* (empty) states, given by (2), are indicated by the $E_i > 0$ line and the σ (occupied) states, from (3) are described by the line where $E_i < 0$. Note that $E_i^\sigma = E_i^{\sigma^*} = E_F$ for maximally coupled sites $C_i = C_{\max}$ by assumption. Since we have not assumed any spectral density depletion near E_F , low energy pair excitations exist at these sites. These processes would presumably contribute to the low temperature thermodynamic measurements. It is worth pointing out that these low energy processes do not necessarily have low transition rates as discussed by Phillips¹⁰ for the general Anderson model since they occur at the same site. Thus the model predicts tunneling states which are localized excitations, at least at low energies.

Also indicated is the absorption energy for a site with lattice coupling C_i according to (5). In the strong coupling case (a) the gap occurs at $E_c - E_v$ as discussed above. Absorption in the weak coupling case (b) occurs initially at C_{\max} where the corresponding one-electron states are localized, indicated by the dark shading for energies less than $E_c - E_v$. Note that one-electron localized states only occur for the weak coupling case. In particular, the number of localized states depends on the strength of the maximum coupling of the system.

It is tempting to apply these considerations to real materials. There is nothing contained within these arguments to limit discussion to semiconductors. Thus all diamagnetic glassy materials will belong to one of two "universality" classes according to the magnitude of their electron-phonon interaction. Chalcogenide glasses, for example, are known to be underconstrained (soft) and are likely strongly coupled systems (in the

sense described in this Comment). The photoconductivity of these systems does indeed mirror the absorption edge in such systems. By contrast, hydrogenated amorphous silicon, which is only marginally diamagnetic (reducing the hydrogen content generally increases the spin density), shows photoconductivity at energies much below the main absorption band. We suggest this is a reflection of the band of localized states which is necessarily evident in weakly coupled materials.

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Figure Captions

Fig. 1. Energy - configuration diagram for the bonding state σ with electronic occupation $n_i^\sigma = 1$, labeled (1) or $n_i^\sigma = 2$, (2) and the antibonding state σ^* with occupation $n_i^{\sigma^*} = 0$, (0) or $n_i^{\sigma^*} = 1$, (1). The arrows refer to the photoabsorption process whereby an electron is transferred from σ to σ^* .

Fig. 2. The correlation between the one-electron energy E_i and the lattice interaction parameter C_i . The absorption energy for sites with lattice parameter C_i is given by the gap in the shading. The (dark) shading corresponds to localized states.

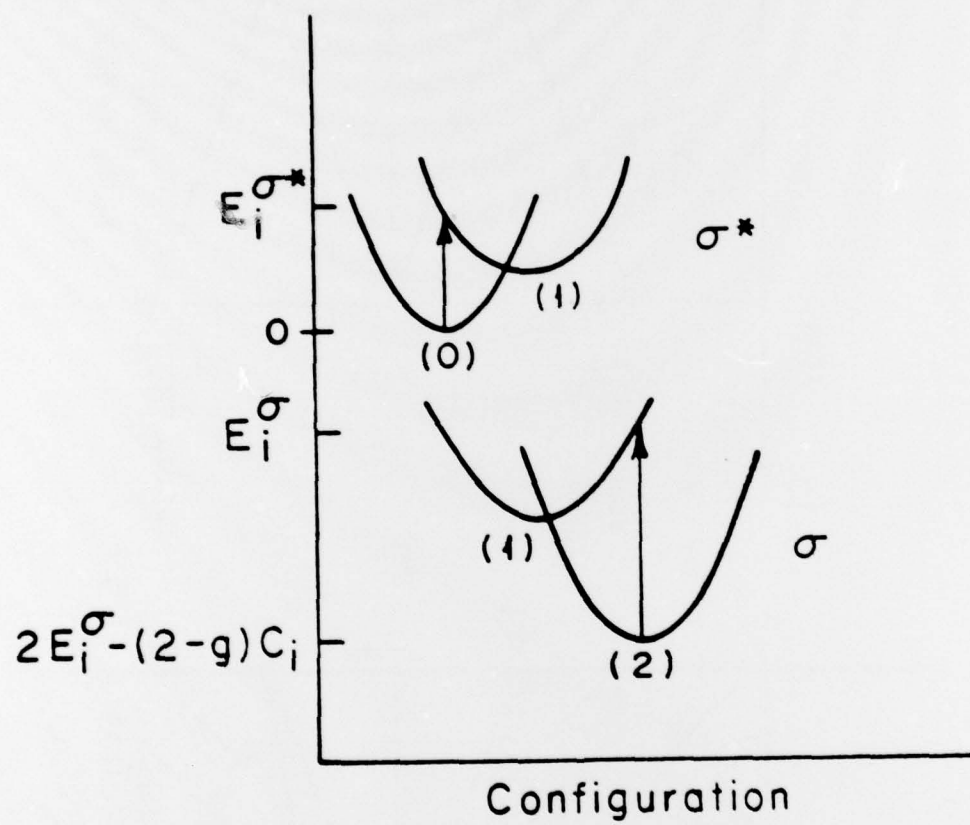


Figure 1.

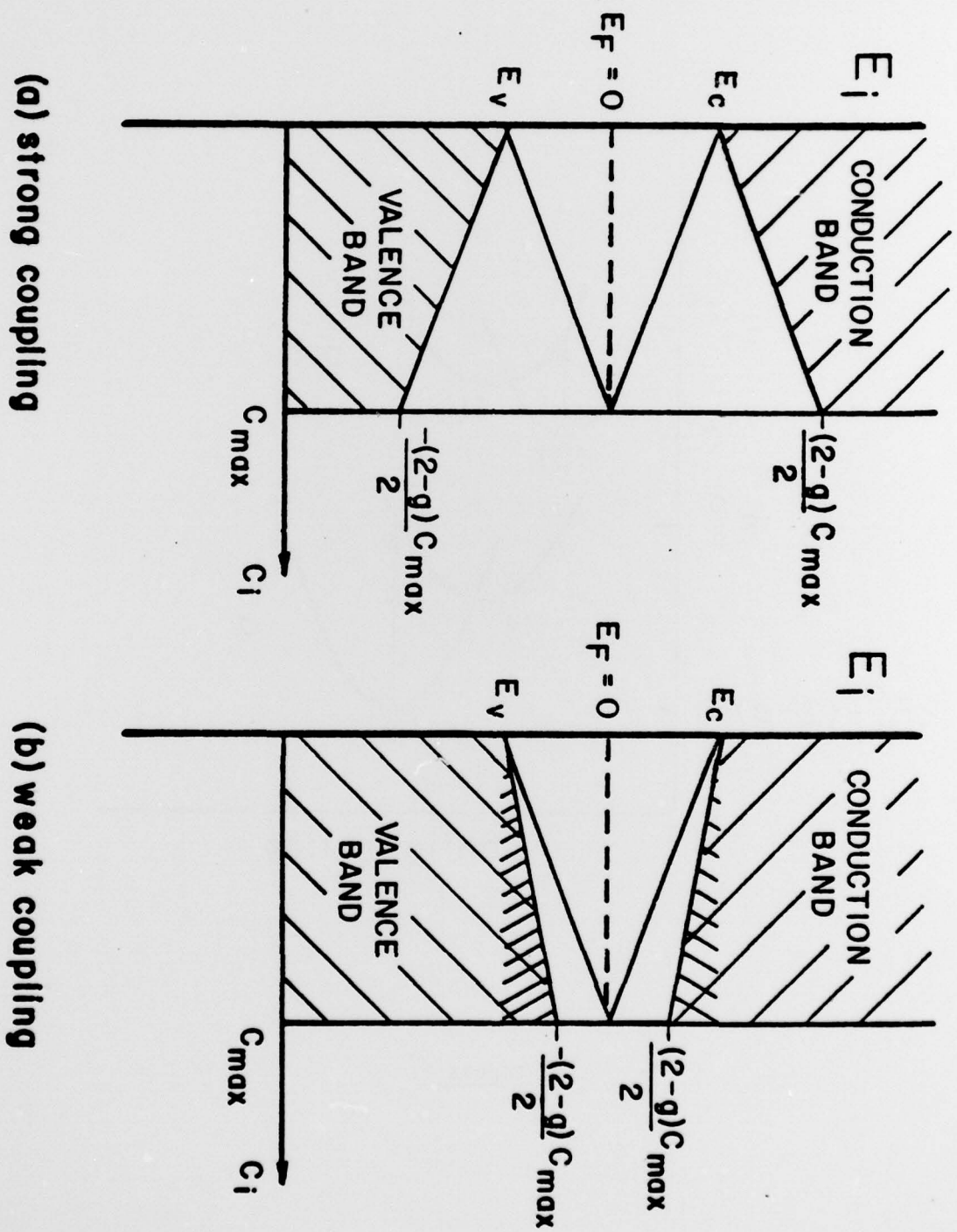


Figure 2

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